# RADIATION SENSITIVE RESIN COMPOSITION AND PATTERN FORMING METHOD USING THE SAME

**Patent number:** JP7159997

**Publication date:** 1995-06-23

**Inventor:** SAKATA YOSHIKAZU; others: 01

**Applicant:** OKI ELECTRIC IND CO LTD

**Classification:**

**- international:** G03F7/038; G03F7/004; G03F7/021; G03F7/028; G03F7/039; G03F7/20; G03F7/26; G03F7/40; H01L21/027

**- european:**

**Application number:** JP19930306954 19931208

**Priority number(s):**



Abstract of **JP7159997**

PURPOSE:To obtain a radiation sensitive resin compsn. developable with water and having higher sensitivity than a conventional compsn.

CONSTITUTION:This radiation sensitive resin compsn. contains 144g (1mol) polyvinyl alcohol deriv. having OH groups each protected by a substituent releasable by an acid, e.g. a t-butoxycarbonyloxy group and 8.25g (0.02mol) acid generating agent which generates the acid under exposure, e.g. triphenylsulfonium triflate.

JAPANESE [JP,07-159997,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM OPERATION EXAMPLE

[Translation done.]



CLAIMS

[Claim(s)]
[Claim 1] The radiation sensitivity resin constituent characterized by including the polyvinyl alcohol derivative from which the OH radical is protected by the substituent from which it can be desorbed with an acid, and the acid generator which generates an acid by exposure.
[Claim 2] The radiation sensitivity resin constituent characterized by showing said polyvinyl alcohol derivative by following the (1) formula in a radiation sensitivity resin constituent according to claim 1 (however, R in (1) type is the substituent from which it can be desorbed with an acid, and the rate of installation is at least 30%.) Moreover, n is a positive integer. .
[Formula 1]

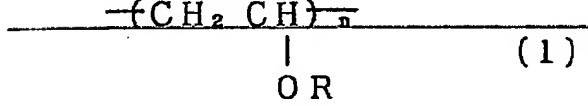
(1)

[Claim 3] The pattern formation approach characterized by including the process which forms the film of a radiation sensitivity resin constituent according to claim 1 or 2 on a substrate, the process which irradiates a radiation alternatively at this film, the process which heat-treats a sample [ finishing / this radiation irradiation ], and the process which develops the film of a sample [ finishing / this heat-treatment ] bywater.
[Claim 4] The pattern formation approach characterized by including the process which irradiates a radiation completely, and the process which heat-treats the sample which irradiated the radiation all over this in the pattern obtained by the pattern formation approach according to claim 3.
[Claim 5] The laminating of a lower layer resist and the upper resist which has absorption to the wavelength field which this lower layer resist does not expose is carried out on a substrate.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the pattern formation approach using a radiation sensitivity resin constituent and this suitable as a component of a resist used for formation of manufacture of a semiconductor device etc. especially an active element, and a circuit pattern.
[0002]
[Description of the Prior Art] When forming detailed processing and a detailed pattern in various fields including the manufacture field of a semiconductor device, the radiation sensitivity resin constituent ******** resist is used abundantly. for example, substrate processing in manufacture of a semiconductor device, for example, formation of the circuit pattern in a semiconductor integrated circuit, -- facing -- the whole processed substrate top surface -- wiring formation -- public funds -- a group thin film is formed and the resist film is formed on this thin film. Furthermore, this resist film is alternatively exposed by the radiation, and is developed after that, and a resist pattern is formed. And this resist pattern is used as a mask, said metal membrane for wiring formation is etched alternatively, and desired wiring is formed. As a conventional sensitive resin constituent which can be used as such a resist, there are some which were indicated by for example, the reference I (the journal OBU vacuum Science technology (Journal of vacuum Science Technology) (6) B8, 1990, pp.1428-1431). This constituent consisted of Pori (4-t-butoxy cull BONIROKISHI styrene-sulfone) and triphenylsulfonium triflate (Ph3 S+AsF6-). This is about 30 mJ/cm2 by exposure by Deep-UV light. It was what can resolve 0.5-micrometer Rhine and a tooth-space (last shipment) pattern by sensibility. Moreover, as a radiation sensitivity resin constituent of usable marketing, it is micro POJITTO 2400 (trade name.) at current production level. The product made from SHIPURE, OEBR-1000 (trade name.) There is TOKYO OHKA KOGYO CO., LTD. make etc. Micro POJITTO 2400 is a resist for MID-UV (light with a wavelength of 280-320nm), and OEBR-1000 are a resist for electron rays.
[0003] On the other hand, in order to attain high integration and improvement in the speed of a semiconductor integrated circuit (IC), detailed-izing of wiring and multilayering are advanced in manufacture of IC. However, since it tends to make the aspect ratio of wiring high and such wiring is multilayered in order to prevent the increment in the wiring resistance by detailed-izing, the level difference on a processed substrate becomes still larger. Therefore, since the above-mentioned level difference comes to cross the range of the depth of focus of an aligner when using for example, a contraction projection aligner and forming a resist pattern on the processed substrate which has such a level difference, by the patterning approach using much more resist like before, there is a possibility that it may become impossible to form a desired pattern. Since there is an inclination for the contraction projection aligner equipped with a lens with large numerical aperture to be used and the depth of focus becomes still shallower in a submicron field especially, this problem becomes still more remarkable.
[0004] Then, it is for example, a reference II:"journal as a technique which solves this. OBU vacuum There was the pattern formation approach called the PCM method of an indication by the Science technology (Journal of vacuumScience Technology), 16(6) Nov./Dec.1979, and pp.1669-1671. It seems that this approach is explained below.
[0005] First, the 1-3-micrometer thick lower layer resist which carries out flattening of this is applied on the processed substrate which has a level difference, and the upper resist as a imaging layer with a thickness of 0.2-0.5 micrometers is applied on this lower layer resist. Next, the upper resist is exposed by an electron ray or near-UV light, negatives are developed after that, and the upper resist pattern is obtained. Next, Deep-UV light is completely irradiated from this upper resist upper part to a lower layer resist by using this upper resist pattern as a mask, after that, a lower layer resist is developed and a bilayer resist pattern is obtained. According to this reference II, PMMA is used as a lower layer resist, and it is AZ1350J (trade name.) as an upper resist. The Hoechst A.G. make is used. Moreover, the upper resist is 5-30microC/cm2 at this time. It is exposed and lower layer resists are 500 mJ/cm2. It is exposed. And the resolution at this time was what can resolve a last shipment pattern with 0.85-

micrometer Rhine and a 2.4-micrometer tooth space.
[0006]
[Problem(s) to be Solved by the Invention] However, in the conventional radiation sensitivity resin constituent, if it was in the thing and micro POJITTO 2400 of an indication in Reference I, the alkali solution needed to be used as a developer, and if it was in OEBR-1000, the organic solvent needed to be used as a developer. A radiation sensitivity resin constituent which can be developed without using these since these developers are inherent in the danger and the pollution problem over the body is desired. Moreover, sensibility [ as opposed to the radiation (electron ray) of OEBR-1000 for example ] is 50microC/cm2. Since it was extent, a radiation sensitivity resin constituent of high sensitivity was desired more.
[0007] Moreover, since PMMA made into the lower layer resist in the method of PCM in Reference II had low thermal stability and the sensibility to a radiation was also low, a lower layer resist ingredient also with high sensibility with high and thermal stability was desired rather than those for the PCM methods.
[0008] It is in this application offering a radiation sensitivity resin constituent [ high sensitivity / before / possible / the development whose problem about the danger or the public nuisance over the body it is made in view of such a point, therefore cannot produce the purpose of the first invention of this application easily / and ]. Moreover, the purpose of the second invention of this application is to offer the suitable approach for the pattern formation by the radiation sensitivity resin constituent of the first invention. Moreover, offering the PCM method using an ingredient new as a lower layer resist has the third invention.
[0009]
[Means for Solving the Problem and its Function] In order to aim at achievement of this purpose, according to the radiation sensitivity resin constituent of the first invention of this application, it is characterized by including the polyvinyl alcohol derivative from which the OH radical is protected by the substituent from which it can be desorbed with an acid, and the acid generator which generates an acid by exposure. According to this radiation sensitivity resin constituent, in that exposed part, an acid generator emits an acid. And this acid has protected the OH radical of a polyvinyl alcohol derivative, and a substituent is desorbed from it. Therefore, the part from which the polarity of a part [ that an OH radical is protected as usual in a polyvinyl alcohol derivative ] and the part to which the OH radical was exposed differs arises. And both parts show behavior which is different to a developer at a development process. the part to which the OH radical was exposed in the above-mentioned polyvinyl alcohol derivative -- also taking -- it does not correct but is polyvinyl alcohol. Since polyvinyl alcohol is meltable in water and it dissolves in the partial selection target with which this radiation sensitivity resin constituent was exposed with this water when water is used as a developer, the development by water is attained. Moreover, as well as the case where water is used when a developer is used as an alkali solution, an exposure part dissolves, and when an organic solvent is used as a developer, the part which was not exposed dissolves. It means that production of a negative mold and a positive type is made as for this to arbitration by what is used as a developer (this property is positively used by the following invention [ third ].). Moreover, since the energy of extent which may generate an acid from an acid generator is sufficient as energy required for exposure, sensibility to the radiation of this radiation sensitivity resin constituent is made highly.
[0010] The polyvinyl alcohol derivative as used in the field of this first invention is specifically made with what is shown by the following (1) formula.
[0011]
[Formula 2]



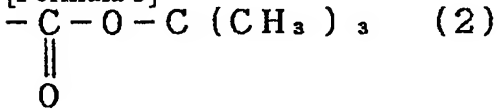
(1)

[0012] However, R in (1) type is the substituent from which it can be desorbed with an acid, and

especially if such, it will not be limited. For example, tertiary butyl [-C (CH3)3] and the t-butoxy cull BONIROKISHI radical shown by following the (2) formula can be used.

[0013]

[Formula 3]



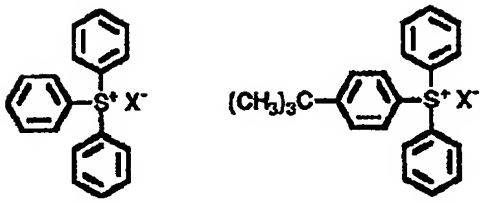
[0014] Any radical is stable at the time of composition of the polyvinyl alcohol derivative concerned, and is because it is that from which it is easily desorbed in an operation of an acid at the time of use. Moreover, considering as at least 30% is suitable for the rate of installation of the substituent R in (1) type. It is because the danger of dissolving in water irrespective of exposing and bending is high when the rate of installation is lower than this. However, since it will be necessary to generate more acids which the desorption of a substituent takes from an acid generator and the sensibility to the radiation of the constituent concerned is made to fall as a result when this rate of installation is too high, this rate of installation of considering and determining these is good.

[0015] Here, the above polyvinyl alcohol derivatives are obtained by protecting the OH radical of commercial polyvinyl alcohol. When for example, t-butoxy cull BONIROKISHI polyvinyl alcohol is considered as a polyvinyl alcohol derivative as used in the field of this invention, that composition can be performed by the synthetic approach by J.M.Frechet of an indication in Reference III (a polymer (POLYMER), Vol.24, p.995 (1983)) etc.

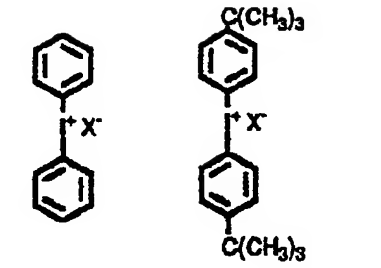
[0016] On the other hand, especially if an acid generator is matter which generates an acid by exposure, it will not be limited. For example, what is listed to a degree can be used. It is TORIKURORO methylation benzene shown by each onium salt shown by the following (3) types and (4) formulas, the sulfonium salt shown in a detail by (3) formulas, the iodonium salt shown by (4) formulas and p-toluene sulfonate shown by following the (5) formula, the TORIKURORO methylation triazine shown by following the (6) formula, and following the (7) formula. Since these generate an acid stronger than a hydrochloric acid, they are suitable.

[0017]

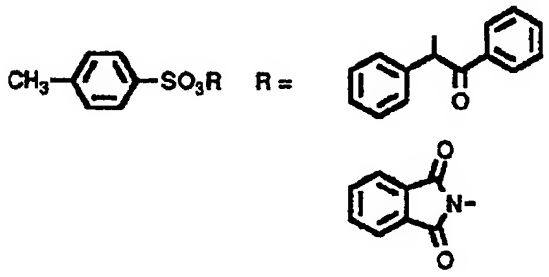
[Formula 4]



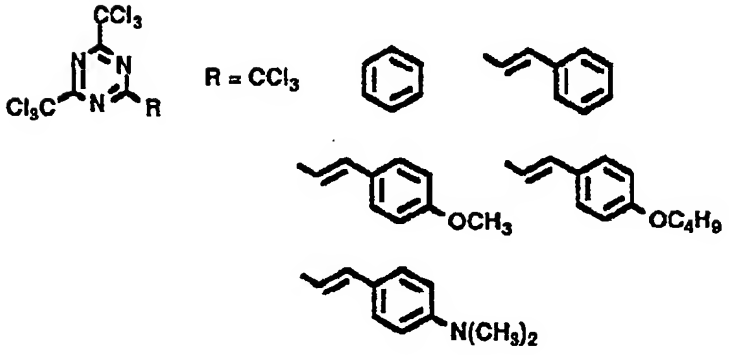

(3)




(4)

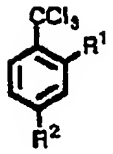


(5)



(6)

[0018]
[Formula 5]



$R^1 = Cl$ $R^2 = Cl$

$R^1 = H$ $R^2 = CCl_3$

( 7 )

[0019] An above-mentioned acid generator [ whether it is marketed and ] Or for example, the approach [journal OBU polymer science by Jay buoy Crivello (J. V.Crivello) etc., Polymer Chemistry Edition (J. Polymer Sci., Polymer Chem. Ed.) 18 or 2677 page (1980)], Tea Approach [journal by ENDO (T. Endo) etc. It is compoundable with OBUPORIMA Science and polymer chemistry edition 23.359-page (1985)].

[0020] 15% of these acid generators are desirable at the maximum to the weight of the polyvinyl alcohol derivative to be used. It is because the acid generator itself will function as a dissolution retardant and it will check the purpose of this invention, in case the exposure part of the constituent concerned is dissolved in water if there are more additions of an acid generator than this amount.

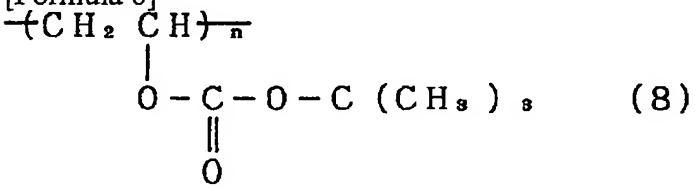
[0021] Moreover, according to the pattern formation approach of the second invention this application, it is characterized by including the process which forms the film of the radiation sensitivity resin constituent of the first invention on a substrate, the process which irradiates a radiation alternatively at this film, the process which heat-treats a sample [ finishing / this radiation irradiation ], and the process which develops the film of a sample [ finishing / this heat-treatment ] bywater. By the pattern formation approach of this second invention, water development can perform desired pattern formation. Moreover, since a sample [ finishing / this exposure ] is heat-treated after exposure, the acid generated from the acid generator in exposure acts effective in a polyvinyl alcohol derivative with the heat at the time of this heat-treatment. According to a design, it can decide on the temperature and time amount of this heat-treatment. However, since the conditions which may promote an operation of an acid are sufficient and it is thought that it is necessary to be neither high temperature nor long duration so much (it is 2 hours at the temperature of 120 degrees C even if it says in the example of the below-mentioned example), it can be said that it is hard to produce the bad influence to the substrate by this heat-treatment (in the heat-treatment after the following exposure, it is the same.).

[0022] In addition, by the pattern formation approach of this second invention, the pattern formed by this approach may be exposed further completely, and a sample [ still finishing / this exposure ] may be heat-treated. If it carries out like this, since all the parts that remained after water development will change to polyvinyl alcohol, a pattern turns into a heat-resistant outstanding pattern more.

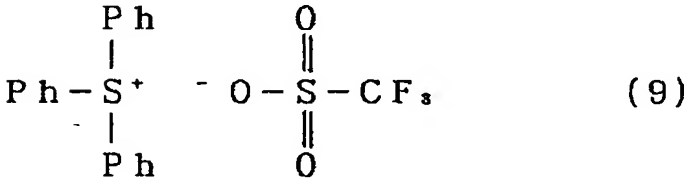
[0023] Moreover, by the pattern formation approach of the third invention this application, it is characterized by using the radiation sensitivity resin constituent of the first invention as a lower layer resist of the PCM method. According to this third invention, the property which the radiation sensitivity resin constituent of the first invention has can be introduced into the PCM method.

[0024] In addition, it is good to heat-treat this sample after an exposure for the 2nd radiation to the account lower layer resist of natural to implementation of this third invention, and to carry out that account development of back to front. It is because the operation to the polyvinyl alcohol derivative of the acid emitted from the acid generator can be promoted. Moreover, it is suitable to form the account of formation back to front upper resist for a barrier layer on said lower layer resist in implementation of this third invention. When the direct laminating of a lower layer resist layer and the upper resist is carried out, the case where the mixing layer resulting from both may arise in both interface, and development is checked as a result arises. It is because a barrier layer prevents generating of the above-mentioned mixing layer. Moreover, a radiation is further irradiated completely to the pattern formed also in the approach of this third invention, and that of a vine is suitable in that treatment of carrying out afterbaking processing. It is because the thermal resistance of a pattern improves like the suitable

example of the second invention.
[0025]
[Example] Hereafter, the example of the first invention of this application - the third invention is explained, respectively. In addition, the material of construction which the following explains and is described and its amount, the processing time, temperature, and other numerical conditions are only the suitable examples of this invention within the limits. Therefore, this invention is not limited only to these conditions.
[0026] 1. Explain the radiation sensitivity resin constituent of the example constituted using the triphenylsulfonium triflate (Ph3 S+OTf-) shown by following the (9) formula as an acid generator using Pori (p-t-butoxy cull BONIROKISHI vinyl alcohol) shown by following the (8) formula as an explanation polyvinyl alcohol derivative of the example of the first invention and the second invention.
[0027]
[Formula 6]

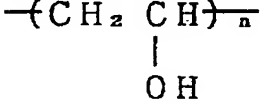


(8)



(9)

[0028] 1-1. **** of the synthetic example of the used polyvinyl alcohol derivative -- compound first Pori (p-t-butoxy cull BONIROKISHI vinyl alcohol) used as a polyvinyl alcohol derivative as follows.
[0029] The suspension which put in and constituted polyvinyl alcohol 44g (one mol) shown by following the (10) formula and t-butoxy potassium 224g (two mols) in Desiccation THF (tetrahydrofuran) is stirred under a room temperature and nitrogen-gas-atmosphere mind.
[0030]
[Formula 7]



(10)

[0031] G t-butyldicarbonate 520g (2.4 mols) is added to this solution, and it stirs for 1 hour. Water is added to this solution and an organic layer is washed with water. This solution is dehydrated with magnesium sulfate, a solvent is distilled off, and objective-tree fat is obtained. This resin When 1 H-NMR analyzed, the peak of the proton of a t-Bu radical was accepted for delta value in 1.6PPM. It was checked from the integrated-intensity ratio of the proton of this t-Bu radical, and the proton of the methyl group of the delta value 3.5 that the rate of installation of the t-Bu radical in this resin is 80%. Moreover, when this resin was analyzed by IR (infrared rays) spectroscopy, the peak of the carbonyl group (-C=O) origin was checked by wave number 1760cm-1. From these things, it was checked that the resin obtained by the above-mentioned composition is Pori (p-t-butoxy cull BONIROKISHI vinyl alcohol).
[0032] 1-2. a radiation sensitivity resin constituent -- Pori (p-t-butoxy cull BONIROKISHI vinyl alcohol) 144g (one mol) which compounded as mentioned above and was obtained, and triphenylsulfonium triflate 8.25g (0.02 mols) -- monochlorobenzene 1780g -- dissolving -- it -- 0.2-

micrometer hole -- filter with a membrane filter and prepare the coating liquid of the radiation sensitivity resin constituent of an example.

[0033] 1-3. Explanation of the Pattern Formation Approach (the 1)

In this case as a substrate, on a silicon substrate, the coating liquid which the above adjusted is applied with a spin coat method, and the film whose thickness is 1.0 micrometers is formed. Next, this film is exposed with various light exposure with the electron ray of conditions with an acceleration voltage of 20kV. A sample [ finishing / exposure ] is heat-treated for 2 minutes at the temperature of 120 degrees C with a hot plate. Next, this sample is developed bywater. It is light exposure 8microC/cm2 It turned out that 0.5micromL/S pattern can be resolved in the conditions carried out.

[0034] 1-4. Explanation of the Pattern Formation Approach (the 2)

the radiation source -- instead of [ of an electron ray ] -- a Xe-Hg lamp -- carrying out -- things -- except conducts a patterning experiment with the procedure of the above-mentioned pattern formation approach (the 1), and the same procedure. At this time, it is light exposure 120 mJ/cm2 It turned out that 0.5micromL/S pattern can be resolved in the conditions carried out.

[0035] 1-5. Explanation of the Pattern Formation Approach (the 3)

The light of a Xe-Hg lamp is irradiated for 5 minutes all over the pattern formed in the procedure of the above-mentioned pattern formation approach (the 1). Next, this sample is heated for 2 minutes at the temperature of 120 degrees C with a hot plate. Deformation of a pattern was not accepted although the sample with which such exposure and heat-treatment were able to be managed was heated in oven with a temperature of 200 degrees C. With the pattern formed in the procedure of the above-mentioned pattern formation approach (the 1), the protective group remains in the extant film. On the other hand, if the radiation irradiation and heat-treatment as used in the field of this term are carried out, a protective group will be removed and a pattern (film) will be formed into poly vinyl alcohol. For this reason, the thermal resistance of a pattern improves.

[0036] 2. Explain the example of explanation of the example of the third invention, next the third invention which uses the radiation sensitivity resin constituent of the first invention as a lower layer resist formation ingredient in the PCM method.

[0037] 2-1. Apply the coating liquid of the radiation sensitivity resin constituent concerning the first invention adjusted in the example of the first and the second invention on the 1st example silicon substrate of the third invention by the rotation applying method, and form the film with a thickness [ of this constituent ] of 1.5 micrometers (formation of a lower layer resist.). This sample is prebaked at the temperature of 60 degrees C using a hot plate.

[0038] Next, the film of polyvinyl alcohol is formed by predetermined thickness as a barrier layer in this case on this lower layer resist.

[0039] Next, by this example, the film of a resist called MP1400 made from SHIPURE is formed by the thickness of 0.2 micrometers as an upper resist on the film of this polyvinyl alcohol. This sample is prebaked at the temperature of 60 degrees C using a hot plate.

[0040] Next, to this sample, the photo mask for a test with the last shipment pattern of various dimensions for the light from the stepper for i lines (numerical aperture = thing of 0.42) is minded from the upper resist upper part, and it is light exposure 200 mJ/cm2. It exposes according to conditions. Even if exposure light results in a lower layer resist (film of the constituent of the first invention) at this time, to i line pan, the light of wavelength, such as g line, does not expose the constituent of the first invention in order not to absorb. Next, a sample [ finishing / this exposure ] is developed with the developer of MP1400 dedication. Since the exposure part of the upper resist is dissolved by exposure here and development, the upper resist pattern of a positive type is obtained by them.

[0041] Next, the package exposure of the light from the aligner of Xe-Hg lamp wearing (however, also a cold mirror equipment) is shortly carried out from the upper resist pattern upper part to this sample. Since MP1400 used as an upper resist here has very large absorption to Deep-UV light (for example, the absorbance in light with a wavelength of 280nm = 2.3), this upper resist pattern serves as an exposure mask of a lower layer resist. Therefore, the part covered by the upper resist of a lower layer resist (film of the constituent of the first invention) is not exposed substantially, but, on the other hand, the part

which is not covered by the upper resist is exposed.
[0042] Next, this sample is heated for 2 minutes at the temperature of 120 degrees C using a hot plate, and negatives are developed for 2 minutes bywater after that. Since the part which is not covered with the upper resist pattern of a lower layer resist is dissolved in this development, the pattern of a positive type is obtained. At this time, it is light exposure 150 mJ/cm2. It turned out that 0.5micromL/S pattern which is the minimum line breadth of the used photo mask for a test is resolved on conditions.
[0043] 2-2. When the pattern finally obtained in the 1st example of the 2nd example of the third invention was heat-treated at the temperature of 200 degrees C, the pattern did not change.
[0044] 2-3. It is an alkali solution (here MF312 (trade name.)) about the developer to be used to having used water as a developer of a lower layer resist in the 1st example of the third 3rd example above-mentioned invention of the third invention. + water made from SHIPURE = it is referred to as 1+20 (volume ratio). A patterning experiment is conducted like the 1st example of the third invention except it. The resist pattern of a positive type was obtained also in this case. Moreover, it turned out that 0.5micromL/S pattern which is the minimum line breadth of the photo mask for a test used also in this case is resolved.
[0045] 2-4. Let the developer to be used be methyl isobutyl ketone (MIBK) which is an organic solvent to having used water as a developer of a lower layer resist in the 1st example of the third 4th example above-mentioned invention of the third invention. A patterning experiment is conducted like the 1st example of the third invention except it. In this case, although MP1400 which is the upper resist dissolves by MIBK and the unexposed part of a lower layer resist (constituent of the first invention) dissolves, the part by which the lower layer resist (film of the constituent of the first invention) was exposed remains. Therefore, the resist pattern of a negative mold is obtained. However, it turned out that 0.5micromL/S pattern which is the minimum line breadth of the photo mask for a test used also in this case is resolved.
[0046]
[Effect of the Invention] Since the development by water is possible, according to the radiation sensitivity resin constituent of the first invention of this application, and the pattern formation approach of the second invention, there are no worries about danger or public nuisance generating to the body, so that clearly also from the explanation mentioned above. Therefore, since the special equipment for waste fluid processing at a development process can be reduced or removed, reduction of the manufacturing cost of a semiconductor device etc. can be aimed at.
[0047] Moreover, since the radiation sensitivity resin constituent of the first invention is a chemistry magnification mold, it becomes what has the high sensibility to a radiation. Moreover, to the light from the source of exposure where current multiple use of polyvinyl alcohol itself is carried out, since permeability is high, a sharp pattern with little pattern sagging is obtained. Moreover, in the radiation sensitivity resin constituent of this first invention, although the development by water is possible like ****, even if based on an alkali solution, negatives can be developed also with an organic solvent. And a positive type pattern is obtained in the development by water and the alkali solution, and a negative-mold pattern is obtained in the development by the organic solvent. For this reason, the free correspondence according to a process is also possible, for example.
[0048] Moreover, the pattern excellent in thermal resistance is obtained with the configuration which exposes completely the pattern which is the second invention and was formed, and heat-treats a sample [ still finishing / this exposure ] (setting to the third invention the same.).
[0049] Moreover, according to the configuration of the third invention, the radiation photopolymer constituent of the first invention is used as a lower layer resist of the PCM method. For this reason, the new PCM method with the description of the sensitive resin constituent of the first invention is realized. Moreover, by the approach of this third invention, since a two-layer resist process can be realized without using the dry etching method, simplification of a process can be attained compared with the two-layer resist method using a dry etching process. Moreover, with the configuration which heat-treats [ which heat-treats and is exposed completely ] the pattern which is the third invention and was formed, the pattern excellent in thermal resistance is obtained like the suitable example of the second invention.

[Translation done.]